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(71)Applicant : HITACHI METALS LTD
(72)Inventor : SHINDO MIKIO
SAKUMA AKIMASA

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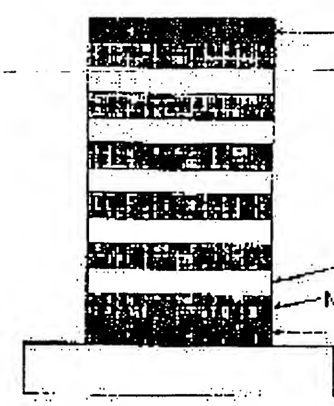
(54) THIN FILM MAGNET, R-TM-B EXCHANGED SPRING MAGNET AND MANUFACTURING METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a thin film magnet having a high max. energy product by laminating a soft magnetic layer having specified magnetization value on a hard magnetic layer contg. specified amt. of rare earth element(s), B and Fe or Fe partly substituted with Co and inevitable impurities.

SOLUTION: Laminating an S layer (soft magnetic layer having a magnetization of 1.3T or more) on an H layer (hard magnetic layer contg. R (at least one of rare earth elements, incl. Y) 10-20at%, B 5-20at%, TM (Fe or Fe partly substituted with Co) and inevitable impurities) produces a thin film magnet. The S and H layers are pref. alternately laminated to form a multilayer film pref. having at the outermost surface an M layer (composed of at least one of Cr, Ti, W, Ta, FeMn, NiMn, Nip, Fed, Cod, Co-Pt and Fe-Pt, thereby suppressing oxidation of the S and H layers.



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* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to a R-TM-B system exchange spring magnet and its manufacture method at the thin film magnet row of the multilayer structure to which the laminating of the R-TM-B system hard magnetism layer applied to a small motor, a magnetometric sensor, an actuator, etc. and the soft-magnetism layer was carried out.
[0002]
[Description of the Prior Art] Corresponding to small and lightweight-izing of an electronics device, highly efficient-ization of permanent magnet material is advanced. An exchange spring magnet is mentioned as an example of the material which may exceed the magnetic properties of the R-TM-B system magnet which has the highest magnet property now. An exchange spring magnet is a permanent magnet which consists of super-fine crystal organizations which consist of a two phase of a hard magnetism phase and a soft-magnetism phase. Coehoorn etc. (J. dePhys.vol.49, p669 (1988)) etc. -- Kneller It is proposed. etc. (IEEE Trans.Mag.vol.27, p3588 (1991)) etc. -- A high energy product will be acquired by combining the large soft-magnetism phase of magnetization, and a hard magnetism phase with large coercive force, and combining these magnetically by the exchange interaction. Magnetization of a hard magnetism phase fixes magnetization of a soft-magnetism phase, and the coercive force of an exchange spring magnet discovers it by barring the flux reversal of a soft-magnetism phase. In order to obtain sufficient coercive force, it is required that the soft-magnetism phase and the hard magnetism phase are carrying out switched connection strongly and for the size (particle size) of each phase to be nano level size. The manufacture method of this exchange spring magnet has a method in use of obtaining the polycrystal which manufactured the amorphous thin band by the super-quenching method, and the soft-magnetism phase and the hard magnetism phase mixed with heat treatment. However, the manufacture method of an exchange spring magnet of depositing a soft-magnetism phase and a hard magnetism phase with heat treatment of an amorphous thin band has the problem that it is very difficult to control the organization.
[0003]
[Problem(s) to be Solved by the Invention] this invention provides with a R-TM-B system exchange spring magnet and its manufacture method the thin film magnet row which has a big maximum energy product by having big magnetization.
[0004]
[Means for Solving the Problem] In an exchange spring magnet, if there is a soft-magnetism phase which carries out switched connection to a hard magnetism phase, flux reversal will begin from a soft-magnetism phase previously under an opposing magnetic field, and it will become the key factor of a coercive force fall. However, if the size of a soft-magnetism phase is held down to below magnetic-domain-wall width of face, the uneven flux reversal under an opposing magnetic field will be suppressed. Consequently, coercive force is mainly governed by the magnetic anisotropy of a hard magnetism phase, and a fall is suppressed. What is necessary is on the other hand, to raise the volume

ratio of a soft-magnetism phase and for that just to make size of one hard magnetism phase as small as possible, in order to obtain the higher flux density B from a soft-magnetism phase. Although the size of a hard magnetism phase should just be below magnetic-domain-wall width of face too, since it will become difficult to maintain coercive force if not much narrow, it is desirable to hold down to a magnetic-domain-wall width-of-face grade. Since magnetic-domain-wall width of face is estimated by pi(A/K) 1 / 2 (A:exchange SUTIFFUNESU constant, K:anisotropy energy), if a soft-magnetism phase is set to Fe and a hard magnetism phase is set to Nd2Fe14B, it will be set to 60nm and about several nm, respectively. R. According to Skomski andJ.M.D.Coey (Phys.Rev.B48(1993) p15812), in an exchange spring magnet, the volume ratio fh of a hard magnetism phase in case maximum energy product (BH) max becomes the largest is given by (1) formula in approximation, and a maximum energy product serves as (2) formulas at this time.

[0005]

$$f_h = \frac{\mu_0 M_s^2}{4 K_h} \qquad (1)$$

（M_s：軟磁性相の磁化、K_h：硬磁性相の磁気異方性エネルギー）

$$(BH)_{max} = \frac{\mu_0 M_s^2}{4} \left(1 - \frac{\mu_0 (M_s - M_h) M_s}{2 K_h}\right) \qquad (2)$$

（M_h：硬磁性相の磁化）

[0006] To the anisotropy energy Kh of Sm-Co or a Nd-Fe-B magnet being about three 107 J/m, since mu0Ms 2/4 of soft magnetic materials, such as Fe, is about three 106 J/m, it should just have about 10% of volume ratios fh of a hard magnetism phase. Therefore, (BH) max serves as the form where the property of a soft-magnetism phase mainly rules over, and slight amendment joins mu0Ms 2/4 quantitatively. (2) When Nd2Fe14B is made into a hard magnetism phase and Fe is made into a soft-magnetism phase in a formula, (BH) max=0.8 MJ/m3 (100MGOe) is expected at fh=10%. In order to acquire the above properties, it has magnetic combination with a hard magnetism phase and a soft-magnetism phase sufficient by the contact interface, and needs to be controlled by the magnetic-domain-wall width-of-face grade which each **** mentioned above. The cascade screen considered this invention person etc. that such control is the structure which may be realized most easily. Moreover, it hit on an idea for the hard magnetism layer which consists of R-TM-B to prevent the fall of coercive force, when it becomes, or this invention person etc. forms the protective coat for the oxidization suppression by thin-film-izing that it will be hard to generate R2TM14B if corrosion resistance is bad and does not fully suppress oxidization, since possibility that switched connection with a soft-magnetism phase will become inadequate, and coercive force will deteriorate is high. Therefore, this invention is the thin film magnet which carried out the laminating of S layers (soft-magnetism layer whose size of magnetization is more than 1.3T), and the H layers (hard magnetism layer containing R (R is at least one sort in the rare earth elements containing Y) which is 10 - 20at%, 5 - 20at% B, Remainder TM (that by which TM replaced a part of Fe or Fe by Co), and an unescapable impurity). Moreover, this invention is the R-TM-B system exchange spring magnet which carried out the laminating of S layers (soft-magnetism layer whose size of magnetization is more than 1.3T), and the H layers (hard magnetism layer containing R (R is at least one sort in the rare earth elements containing Y) which is 10 - 20at%, 5 - 20at% B, Remainder TM (that by which TM replaced a part of Fe or Fe by Co), and an unescapable impurity).

[0007] In this invention, in order to carry out switched connection of S layers and the H layers, it is desirable to carry out the laminating of S layers and the H layers by turns, and to consider as a multilayer. Moreover, it is desirable to form M layers (layer which consists of one sort or two sorts or more in Cr, Ti, W, Cu, Ta, FeMn, NiMn, NiO, FeO and CoO, Co-Pt, and Fe-Pt) in the outermost side of the multilayer which carried out the laminating of S layers and the H layers, and to suppress oxidization of S layers and H layers.

[0008] In this invention, H layers are hard magnetism layers containing a 10 - 20at% R (R is at least one sort in the rare earth elements containing Y), 5 - 20at% B, Remainder TM (that by which TM replaced a part of Fe or Fe by Co), and an unescapable impurity. Especially as R, it is desirable to include at least one sort of Nd or Pr, and a part of Nd or Pr may be replaced by Dy. As for H layers which consist of R-TM-B, it is desirable for thickness to be 5-100nm including R2TM14 B phase. R of H layers is not 5-100 10^{-10} m = [coercive force sufficient less than / 10at%] discovered, more than at 20at%, Fe component decreases and Br decreases as (BH) max. Less than [5at%], coercive force declines, and, as for B, Br falls as (BH) max more than at 20at%. Moreover, if a kind of element of Cr, Nb, aluminum, Ga, Zn, and Cu is added at least to H layers, although a R-TM-B system exchange spring magnet with still more sufficient coercive force and square shape nature can be obtained, since Br will fall as (BH) max if it adds .0005-.0100 10^{-6} m exceeding 4at%, you may be less than [4at%].

[0009] Since the magnetization of H layers which consists of R-TM-B is usually more than 1.3T at a room temperature, in order to acquire the predominance of an exchange spring magnet, in order to carry out to more than 1.3T at a room temperature and to exceed the property of the R-TM-B system magnet of bulk further, as for the size of magnetization of S layers, it is desirable to carry out to more than 1.5T. As soft magnetic materials beyond 1.3T, Fe:2T, Fe-Co:2.3T, and Fe-N:2.4T grade have the size of the magnetization in a room temperature. As for S layers, it is desirable to think from the width of face of the magnetic domain wall, and to have the thickness of the range of 5nm - 500nm. Although the multilayer which carried out the laminating of S layers and the H layers by turns is formed in order to carry out switched connection of H layers and the S layers Even if the order of a laminating carries out a laminating to S layers, H layers, and S layers ... S layers, it carries out a laminating to H layers, S layers, and H layers ... H layers, it carries out a laminating to S layers, H layers, and S layers ... H layers and it carries out a laminating to H layers, S layers, and H layers ... S layers, any are sufficient as

[0010] M layers are formed in the outermost side of the multilayer which carried out the laminating of S layers and the H layers by turns, and oxidization of S layers and H layers is controlled. You may fabricate M layers at one of the two so that you may form all over an outermost side and a multilayer may be inserted. Although the effect of oxidization control is acquired also by forming M layers between a substrate and a multilayer and in either on the multilayer of S layers and H layers, if it forms so that the whole outermost side surface or a multilayer may be inserted, it can be alike, and oxidization of S layers and H layers can be controlled more enough, consequently the switched connection of H layers and S layers becomes strong, and the multilayer which was excellent in magnetic property can be obtained. Moreover, the effect of preventing a reaction with oxidization control of S layers or H layers and a substrate is acquired by forming M layers on a substrate and carrying out the laminating of the multilayer of S layers and H layers on it. 5nm - 100nm of thickness of M layers is desirably set to 5-20nm so that the function may not fully be spoiled, even if it forms an alloy or a compound by the interface according to counter diffusion with H layers which adjoin this, or S layers.

[0011] Since NiO, FeO, and CoO are antiferromagnetism insulators, if this is used as M layers, in addition to the effect of oxidization suppression, the effect of the improvement in coercive force can be acquired by stopping flux reversal. since it compares with other M lamination matter and there are few antioxidizing effects although the effect of the improvement in coercive force can be acquired if this is used as an M layer, since FeMn and NiMn are also the antiferromagnetic substance, it is desirable to form between a substrate, H layers, or S layers Moreover, since Co-Pt and Fe-Pt are ferromagnetic metals which have a strong crystal magnetic anisotropy, if this is used as M layers, in addition to the antioxidizing effect and the effect of coercive force increase, they can also expect increase of magnetization.

[0012] Although it is desirable to form membranes at the substrate temperature below 773K (500 degrees C) as for H layers in order to suppress the oxidization at the time of membrane formation of H layers, it has become amorphous, without H layers which consist of R-TM-B in that case crystallizing R2TM14B, and coercive force is not discovered. In this case, heat treatment is required in order to obtain the polycrystal of R2TM14B. Since R2TM14B will not crystallize heat treatment temperature if it is made below into 773K (500 degrees C), if coercive force is not discovered and it carries out more than

1073K (800 degrees C), coercive force will decrease rapidly. Therefore, although 773K (500 degrees C) to 1073K (800 degrees C) are suitable for heat treatment temperature, there is little disorder of the laminated structure by the diffusion under heat treatment, and 773K (550 degrees C) to 923K (650 degrees C) which R2TM14B generates enough are desirable.
[0013]
[The mode of implementation of invention]
(Example 1) The inside of the vacuum tub of bipolar magnetron-sputtering equipment was exhausted to 8x10 - 4 or less Pa, and Ar gas was introduced, it was referred to as 8x10 to 1 Pa, high-frequency voltage was impressed to a Nd-Fe-B alloy target which becomes the film composition of H layers indicated to the claim 1, and membranes were formed on the glass substrate of a room temperature. After it set injection power to 200W, it performed reserve sputtering for 20 minutes where the shutter attached between the substrate and the target is closed, and it removed the oxide on a target front face etc., it opened the shutter and formed 20nm of Nd-Fe-B films. Film composition of a Nd-Fe-B film monolayer is Nd13 - 15FebalB 7-11 (at%), and membrane formation speed is 2.0 micrometer/hour. Without breaking a vacuum succeedingly, high-frequency voltage was impressed to Fe target, and 20nm of Fe films was formed on the same membrane formation conditions as Nd-Fe-B. Membrane formation speed is 0.3 micrometer/hour. By repeating this by turns, the multilayer of Nd-Fe-B and Fe was produced (laminating period 5), and, finally the Nd-Fe-B film was formed. The obtained Nd-Fe-B/Fe multilayer was heat-treated by 873K (600 degrees C) in 30 minutes and in the vacuum of 3x10 - 3 or less Pa.
[0014] (Example 2) 20nm of Ti was formed on the glass substrate, the Nd-Fe-B/Fe multilayer same next as an example 1 was formed, finally 20nm of Ti was formed, and it considered as Ti/(Nd-Fe-B/Fe)5 / a Nd-Fe-B/Ti cascade screen like drawing 1 . The membrane formation conditions of Ti are the same as that of Fe and Nd-Fe-B, and membrane formation speed is 1.3 micrometer/hour. The obtained film was heat-treated on (an example 1) and these conditions.
[0015] (Example 3) The Nd-Fe-B/Fe multilayer same on a glass substrate as (an example 1) was formed, and, finally 20nm of Ti was formed. That is, the film which does not have Ti layer between a glass substrate and a Nd-Fe-B/Fe multilayer as compared with (an example 2) was produced. The obtained film was heat-treated on (an example 1) and these conditions.
[0016] (Example 4) 20nm of Ti was formed on the glass substrate, and the same Nd-Fe-B/Fe multilayer as succeedingly (example 1) was formed. That is, the film which does not have Ti layer on a Nd-Fe-B/Fe multilayer as compared with (an example 2) was produced. The obtained film was heat-treated on (an example 1) and these conditions.
[0017] The demagnetization curve of the film obtained in the examples 1-4 is shown in drawing 2 . An example 2 has the largest coercive force. It is thought that the coercive force of a twist did not discover the example 1 to oxidization of Nd-Fe-B layer. Although examples 3 and 4 have coercive force larger than an example 1, as compared with an example 2, coercive force declines a little. From these results, a Nd-Fe-B/Fe multilayer is understood that protective layers, such as Ti, are required between a substrate and multilayers or for at least the front face (topmost part) of a multilayer either, and protective layers, such as Ti, are required between a substrate and multilayers and for the front face (topmost part) of a multilayer desirably. In order to investigate the springback property of the film obtained in the examples 1 and 2, the minor loop at the time of repeating impression of a demagnetizing field and removal of a demagnetizing field is shown in drawing 5 and drawing 6 . The springback of magnetization of the film obtained from drawing 5 in the example 1 was not accepted. On the other hand, when drawing 6 was seen, since the springback of the magnetization which magnetization recoils was accepted even if it impressed the demagnetizing field, the film obtained in the example 2 has checked that it was the exchange spring magnet in which H layers and S layers carried out switched connection. From this, in order to carry out switched connection of H layers and the S layers, it is thought effective to form protective layers, such as Ti.
[0018] (Example 5) In the Ti/(Nd-Fe-B/Fe) 5-/Nd-Fe-B/Ti cascade screen of an example 2, heat treatment temperature was changed from 673K in 1123K (from 400 degrees C to 850 degrees C). The

heat treatment temperature dependence of coercive force is shown in drawing 3 . Coercive force sufficient by below heat treatment temperature 773K (500 degrees C) is not discovered, and deformation of a substrate and degradation of a rapid property are caused above 1073K (800 degrees C). Therefore, heat treatment temperature needs to be the range of 773K to 1073K (from 500 degrees C to 800 degrees C), and its range of 823K to 923K with still larger coercive force (from 550 degrees C to 650 degrees C) is desirable.

[0019] (Example 6) Other conditions produced the Cr/(Nd-Fe-Cr-B/Fe) 5-/Nd-Fe-Cr-B/Cr cascade screen by the same method as an example 2 using the Nd-Fe-B alloy target containing Cr (film composition of a Nd-Fe-Cr-B film monolayer is Nd13-15FebalB7-11Cr 0.5-1.5 (at%)). The obtained film was heat-treated like (the example 1). A demagnetization curve is shown in drawing 4 as compared with (an example 2). The direction at the time of adding Cr in Nd-Fe-B layer can obtain the good thin film magnet of coercive force and square shape nature. This effect was the same also at the case of Nb, aluminum, Ga, Zn, and Cu.

[0020] (Example 7) On the glass substrate, M 15nm layers shown in Table 1 were formed, except having considered as the film composition which shows film composition in Table 1 below, 5 (Nd-Fe-B/S)/Nd-Fe-B was formed on the same conditions as an example 1, and M 15nm layers further shown in Table 1 were formed. Nd-Fe-B layer thickness and thickness of S layers were set to 15nm and 50nm, respectively. The obtained cascade screen was heat-treated at 570 degrees C - 600 degrees C in 30 minutes and in the vacuum of 3x10 - 3 or less Pa. The magnetic properties of the obtained magnet are shown in Table 1.

[0021]

[Table 1]

試料No	積層膜				磁気特性		
	基板上M層	H層 (Nd-Fe-B層)	S層	M層	Br (T)	iHc (KA/m)	(BH)max (KJ/m³)
1	Ti	$Nd_{14}Fe_{77}B_9$	Fe	Ti	1.4	656.3	200.2
2	Cu	$Nd_{12}Dy_2Pe_{59}Co_{18}B_9$	$Pe_{66}Co_{34}$	Ta	1.3	803.1	195.1
3	Cr-Ta	$Nd_{13}Fe_{73}Cr_5B_9$	Fe	Cr	1.3	741.5	190.5

[0022] (Example 8) On the glass substrate, M 15nm layers shown in Table 2 were formed, except having considered as the film composition which shows film composition in Table 1 below, 5 (Nd-Fe-B/Fe)/Nd-Fe-B was formed on the same conditions as an example 1, and M 15nm layers further shown in Table 2 were formed. Nd-Fe-B layer thickness and thickness of S layers were set to 15nm and 50nm, respectively. The obtained cascade screen was heat-treated at 600 degrees C - 620 degrees C in 30 minutes and in the vacuum of 3x10 - 3 or less Pa. The magnetic properties of the obtained magnet are shown in Table 2.

[0023]

[Table 2]

試料No	積層膜				磁気特性		
	基板上M層	H層 (Nd-Fe-B層)	S層	M層	Br (T)	iHc (KA/m)	(BH)max (KJ/m³)
4	FeMn	$Nd_{14}Fe_{77}B_9$	Fe	Ti	1.4	804.2	190.1
5	NiMn	$Pr_6Nd_7Fe_{78}B_7C_2$	Fe	Ti	1.4	750.2	196.2

[0024] (Example 9) On the glass substrate, M 15nm layers shown in Table 3 were formed, except having considered as the film composition which shows film composition in Table 1 below, 5 (Nd-Fe-B/Fe)/Nd-Fe-B was formed on the same conditions as an example 1, and M 20nm layers further shown in Table 3 were formed. Nd-Fe-B layer thickness and thickness of S layers were set to 15nm and 50nm,

respectively. The obtained cascade screen was heat-treated at 570 degrees C - 600 degrees C in 30 minutes and in the vacuum of 3x10 - 3 or less Pa. The magnetic properties of the obtained magnet are shown in Table 3.

[0025]

[Table 3]

試料No	積層膜				磁気特性		
	皺上M層	H層 (Nd-Fe-B層)	S層	M層	Br (T)	iHc (KA/m)	(BH)max (KJ/m³)
6	NiO	$Nd_{12}Dy_2Fe_{60}Co_{18}B_8$	$Fe_{80}Co_{20}$	NiO	1.4	850.7	205.8

[0026] (Example 10) On the glass substrate, M 15nm layers shown in Table 4 were formed, except having considered as the film composition which shows film composition in Table 1 below, 5 (Nd-Fe-B/Fe)/Nd-Fe-B was formed on the same conditions as an example 1, and M 15nm layers further shown in Table 4 were formed. Nd-Fe-B layer thickness and thickness of S layers were set to 15nm and 50nm, respectively. The obtained cascade screen was heat-treated at 570 degrees C - 600 degrees C in 30 minutes and in the vacuum of 3x10 - 3 or less Pa. The magnetic properties of the obtained magnet are shown in Table 4.

[0027]

[Table 4]

試料No	積層膜				磁気特性		
	皺上M層	H層 (Nd-Fe-B層)	S層	M層	Br (T)	iHc (KA/m)	(BH)max (KJ/m³)
7	Co-Pt	$Nd_{14}Fe_{60}Co_{18}B_8$	$Fe_{80}Co_{20}$	Co-Pt	1.4	911.2	201.3
8	Fe-Pt	$Nd_{14}Fe_{78}B_8$	$Fe_{60}Co_{40}$	Fe-Pt	1.5	880.6	214.5

[Effect of the Invention] By this invention, magnetization is large and the thin film magnet and R-TM-B system exchange spring magnet which have a big maximum energy product are obtained.

[Translation done.]

DESCRIPTION OF DRAWINGS

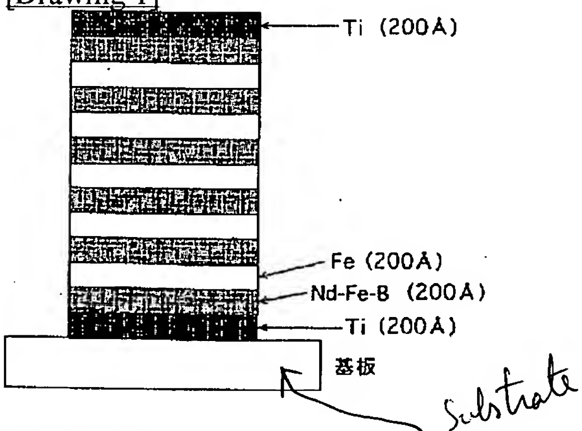
[Brief Description of the Drawings]
[Drawing 1] It is the cross section of this invention exchange spring magnet.
[Drawing 2] It is drawing showing the relation between M layers and a demagnetization curve.
[Drawing 3] It is drawing showing the heat treatment temperature dependence of coercive force.
[Drawing 4] It is a demagnetization curve at the time of carrying out Cr addition at H layers.
[Drawing 5] It is the minor loop which does not show the springback of magnetization.
[Drawing 6] It is the minor loop which shows the springback of magnetization.

[Translation done.]

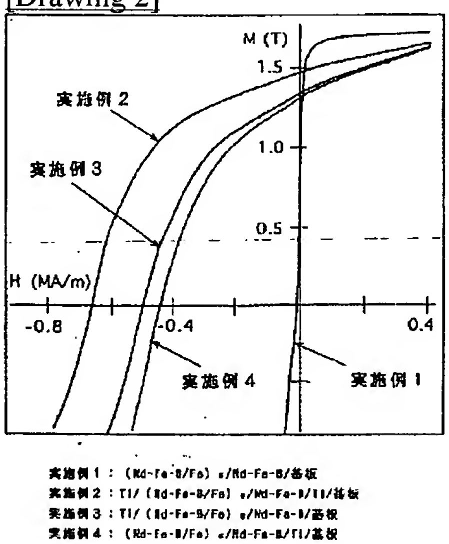
* NOTICES *

DRAWINGS

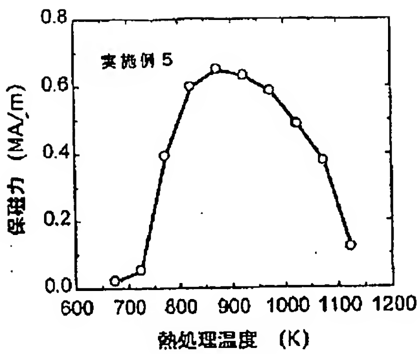
[Drawing 1]



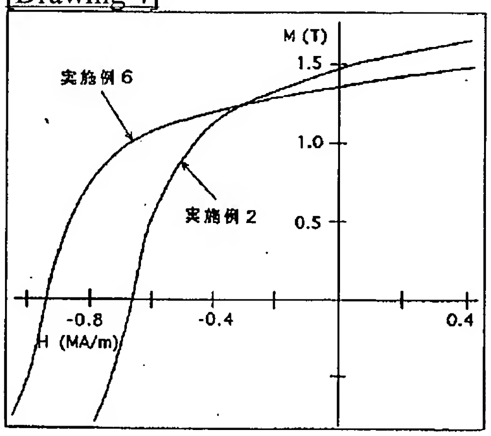
[Drawing 2]



[Drawing 3]

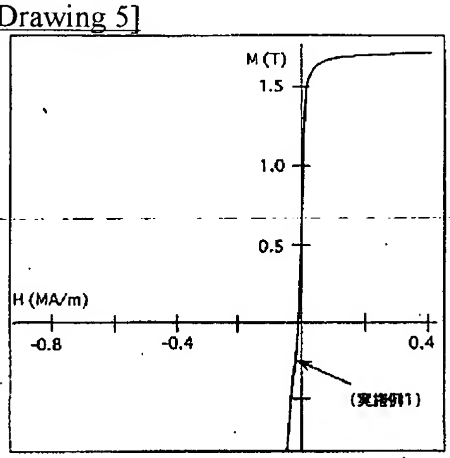


[Drawing 4]



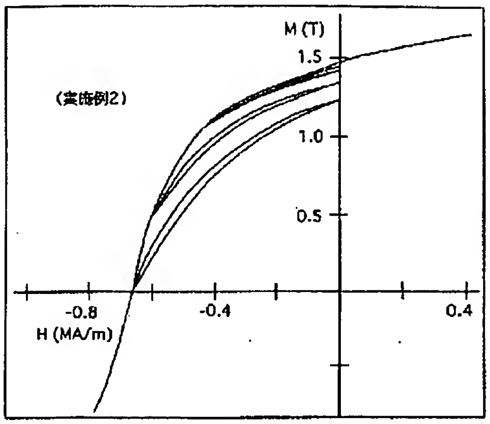
実施例 2 : Ti/(Nd-Fe-B/Fe)$_5$/Nd-Fe-B/Ti/基板
実施例 6 : Cr/(Nd-Fe-Cr-B/Fe)$_5$/Nd-Fe-Cr-B/Cr/基板

[Drawing 5]



(実施例1) (Nd-Fe-B/Fe)*5/Nd-Fe-B/基板

[Drawing 6]



(実施例2) Ti/(Nd-Fe-B/Fe)*5/Nd-Fe-B/Ti/基板

[Translation done.]